

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
7 June 2001 (07.06.2001)

PCT

(10) International Publication Number
WO 01/40178 A1

(51) International Patent Classification⁷: **C07D 201/02**

(21) International Application Number: **PCT/NL00/00879**

(22) International Filing Date:
30 November 2000 (30.11.2000)

(25) Filing Language: Dutch

(26) Publication Language: English

(30) Priority Data:
1013728 2 December 1999 (02.12.1999) NL

(71) Applicant (for all designated States except US): **DSM N.V.**
[NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **LOONTJENS, Jacobus, Antonius** [NL/NL]; Synagogeplantsoen 76, NL-6231 KK Meerssen (NL).

(74) Agent: **MOOIJ, Johannes, Jacobus**; DSM Patents & Trademarks, P.O. Box 9, NL-6160 MA Geleen (NL).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

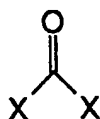
Published:

- With international search report.
- Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/40178 A1

(54) Title: PROCESS FOR THE PREPARATION OF A CARBOXYLIC ACID DERIVATIVE



(I)

(57) Abstract: Process for the preparation of a carboxylic acid derivative according to general formula (I) where the fragments X are a lactam, an oxime or an imide in the form of HX, by mixing HX with phosgene, with hydrogen chloride being removed in gaseous form from the mixture formed. This can be accomplished by not adding any base to the reaction mixture. The invention also relates to carbonylbis caprolactam, characterized in that

the water content is lower than 250 ppm and the chlorine content is lower than 300 ppm. The invention also relates to a process for increasing the molecular weight of a polymer by mixing an -OH- or -NH₂-functional polymer in the melt with a carboxylic acid derivative according to formula (I), characterized in that the carboxylic acid derivative has a water content of less than 250 ppm and a chlorine content of less than 300 ppm.

5 PROCESS FOR THE PREPARATION OF A CARBOXYLIC ACID DERIVATIVE

The invention relates to a process for the preparation of a carboxylic acid derivative according to the following general formula:



where the fragments X are a lactam, an oxime or an imide in the form of HX, by mixing HX with phosgene.

Such a process is disclosed in JP-A-42017832. In the known
15 process a solution of phosgene in benzene is added to a solution of ϵ -caprolactam and triethylamine, also in benzene. In the resulting reaction mixture a precipitate is formed that consists of a mixture of N,N'-carbonylbiscaprolactam and the HCl salt of triethylamine. The HCl salt of triethylamine is removed from a filtrate of the precipitate by washing with water.

20 A drawback of the process disclosed in JP-A-42017832 is that the carboxylic acid derivative precipitate that is formed also contains an HCl salt.

The aim of the invention is to provide a process that does not have this drawback.

This aim is achieved by the hydrogen chloride being removed in
25 gaseous form from the mixture formed. Hydrogen chloride can be removed in gaseous form when no base is used to bind the hydrochloric acid.

An advantage of the invention is that it is not necessary to separate the mixture of the carboxylic acid derivative precipitated during the reaction and the HCl salt. Another advantage is that no base needs to be added,
30 so that the costs of the process according to the invention are lower than those of the known process.

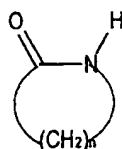
The process according to the invention can be carried out by slowly adding phosgene, which may optionally be present in a first solvent, to a solution of HX in a second solvent. The resulting mixture can be flushed, for
35 instance with a nitrogen flow, for discharge of the hydrochloric acid formed. When

all phosgene has been added, the reaction mixture can slowly be heated, upon which a residual amount of hydrochloric is removed in gaseous form. The hydrochloric acid can be removed by refluxing the reaction mixture under conditions such that phosgene flows back into the reaction mixture. At
 5 atmospheric pressure the reaction mixture is preferably refluxed at a temperature between 0 and 25°C, more preferably between 5 and 15°C. Under pressure higher temperatures can be applied.

Upon completion of the reaction, volatile components such as phosgene, solvent and lactams can be removed, for instance with the aid of a film
 10 evaporator. Oximes and imides can for instance be removed through extraction or fractionated crystallization.

As first and second solvents use can be made of aliphatic aromatic hydrocarbons or ethers. Suitable solvents are toluene and xylene. Preferably, the first solvent is the same as the second solvent.

15 Lactams may be:



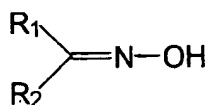
II

with $n = 3-12$.

20 Preferably, use is made of ϵ -caprolactam. This ensures good conversion to carbonylbiscaprolactam and enables the carboxylic acid derivative to be readily purified of any ϵ -caprolactam still present, for instance by means of the aforementioned film evaporation.

A major advantage in the preparation of carbonylbiscaprolactam
 25 according to the invention is that, due to the absence of a base, fewer by-products in the form of nylon oligomers and polymers are formed.

Oximes that can be used have the general formula:

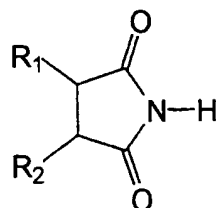


where R_1 and R_2 may be a hydrogen radical, an alkyl radical or an aryl radical. R_1 and R_2 may be the same or different.

$R_1 = H, C_nH_{2n+1}$, with $n = 1-6$ or aryl

$R_2 = H, C_nH_{2n+1}$, with $n = 1-6$ or aryl

- 5 Imides may be aliphatic or aromatic, with the following general formula:



where R_1 and R_2 may be chosen from

- 10 $R_1 = H, C_nH_{2n+1}$ $n = 1-6$ or aryl and $R_2 = H, C_nH_{2n+1}$ $n = 1-6$ or aryl or formula IV is phthalimide

- The carboxylic acid derivatives formed are commonly employed for entering into reactions with hydroxy-functional or amino-functional materials, the reaction temperature depending on the choice of X or, if HX is an oxime or an imide, on the choice of R_1 and/or R_2 , and if HX is a lactam, on the choice of n.
- 15 Carboxy-functional materials may also be present, but take no part in the reaction.

- As already mentioned, it is an advantage of the process according to the invention over the known process that it is not necessary to separate the carboxylic acid derivative precipitated during the reaction and the HCl salt upon completion of the reaction in the process according to the invention.
- 20 The above-mentioned separation is effected by washing with water. Because of the presence of chlorine salts, a residual amount of water as well as chlorine will always remain behind in the carboxylic acid derivative prepared according to the known process.

- 25 An advantage of the process according to the invention is that the carboxylic acid derivative contains less than 250 ppm water and less than 300 ppm chlorine. The chlorine still present in the carboxylic acid derivative may be present in the form of a chlorine salt or in the form of one or more organic chlorine compounds. Refluxing for a sufficiently long time results in a low chlorine content
- 30 and enables better drying of the product, so that the carboxylic acid derivative

according to the invention preferably contains less than 250 ppm chlorine and less than 200 ppm water, more preferably respectively less than 150 ppm chlorine and less than 150 ppm water.

5 With the known preparation and purification methods such as recrystallization, etc., such low amounts of water and chlorine are not achieved. The invention also relates to a carboxylic acid derivative according to general formula I with less than 250 ppm water and less than 300 ppm chlorine.

The invention also relates to a process for increasing the molecular weight of a polymer by mixing an -OH- or -NH₂-functional polymer in
10 the melt with a carboxylic acid derivative according to formula I. Such a process is known from WO-A-98/47940, which discloses that the above-mentioned molecular weight increase, henceforth referred to as chain extension, of -OH- or -NH₂-functional polymers is effected by addition of a carboxylic acid derivative according to formula I to a melt of an -OH- or -NH₂-functional polymer. The
15 temperature of such a melt generally lies between 100 and 350°C.

A drawback of the known process is that the activity of the carboxylic acid derivative with respect to the increase in the molar weight is lower than might be expected on the basis of the amount added. The invention aims to provide a process that does not have the above-mentioned drawback. This is
20 achieved through the use of a carboxylic acid derivative with less than 250 ppm water and less than 300 ppm chlorine. Thus a higher molar weight of the polymer is achieved with the same amount of carboxylic acid derivative. The extra chain extension realized through the use of the carboxylic acid derivative with less than 250 ppm water and less than 300 ppm chlorine is substantially higher than can be
25 explained on the basis of the reduced amounts by weight of water and chlorine. As the water and chlorine content of the carboxylic acid derivative decreases, the amount of carboxylic acid derivative needed for the extension decreases further or, in other words, at equal amounts of carboxylic acid derivative according to the invention the molar weight of the chain-extended polymer increases further.
30 Preferably, a carboxylic acid derivative is used for chain extension that contains less than 150 ppm water and less than 150 ppm chlorine.

Preferably, chain extension is carried out using a bislactam. More preferably, this is carbonylbiscaprolactam.

Chain extension can be carried out in a simple manner using the
35 customary melt mixing techniques and equipment, for instance by mixing of the

lower-molecular functional polymer and the carboxylic acid derivative and optionally further additives in the solid state, for instance in a tumble dryer, following which the resulting mixture is melted in a customary melt mixing device, for instance a Haake kneader, a Brabender mixer or a single- or twin-screw mixer.

5 The various components may also be fed separately to the mixing equipment.

The carboxylic acid derivative can be added to the melted product flow of the functional polymer upon exiting the polymerization reactor, or during a processing step in an extruder. If the carboxylic acid derivative is added to the polymer after exiting the polymerization reactor, the polymerization process
10 can be carried out both batchwise and continuously. In both cases a reduction in the residence time in the reactor can be realized, and hence an increase in productivity. In addition, in these processes according to the invention the post-condensation step can be avoided.

The invention will now be elucidated on the basis of the
15 following examples, without however being limited to these.

Materials used:

Polyethylene terephthalate (PET) with a relative viscosity (η_{rel}) = 1.56, a -COOH terminal group content of 0.030 meq/g and an -OH terminal group
20 content of 0.070 meq/g.

Preparation of carbonyl-bis-caprolactamate

113 g (1 mol) caprolactam is mixed with 200 ml xylene and cooled to 5°C. Over a period of 1 hour 55 g (0.56 mol) phosgene (COCl_2) is
25 introduced into the solution. After that, the solution is stirred for 2 hours at 5°C, while the HCl formed is discharged with the aid of a nitrogen flow. A reflux cooler prevents the removal of phosgene.

Subsequently, the mixture is heated at 40°C for 2 hours and then at 80°C for 2 hours. The mixture is cooled to 50°C and the suspension is
30 three times extracted with 100 ml water. Finally, the suspension is cooled to room temperature and the precipitate, carbonyl-bis-caprolactamate, is isolated by means of filtration. The filtrate is dried overnight under vacuum at 50°C. The melting point of the product is 114.5°C and the chlorine content is 76 ppm and the water content 83 ppm.

35 In the second series the aqueous extraction was carried out only

once. The chlorine content now is 90 ppm and the water content is 135 ppm after drying overnight at 50°C under vacuum.

Carbonylbiscaprolactam obtained according to a known process was washed with water and the washed product was dried overnight under vacuum at 50°C. Depending of the number of washings the product had the water and chlorine contents given in Table 1 under Comparative Experiments 1 and 2.

The PET is melted in a Brabender mixer, type Plasticorder 651, at 280°C until a constant torque of the kneading rods is reached, then carbonylbiscaprolactam is added and mixing is continued. The torque of the kneading rods is measured at different points of time. Mixing is effected at a kneading rod speed of 30 revolutions per minute and under a nitrogen blanket to prevent oxidation-induced PET decomposition. After 5 minutes the polymer is removed from the kneader and the relative viscosity is determined in o-cresol.

Table 1 presents the compositions examined and the results of the measurements.

The results of Examples 1 and 2 versus the Comparative Experiments 1 and 2 prove that the activity of the carbonylbiscaprolactam is surprisingly high, with the low water and chlorine content on account of which a higher viscosity is achieved, which is not the case when use is made of the carbonylbiscaprolactam according to the state of the art.

A higher activity in practice makes it possible to realize a stable higher melt viscosity or an increase in the molar weight of PET when use is made of a bislactam.

Table 1

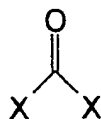
Experiment/Composition	Example 1	Example 2	Comp. Exp. 1	Comp. Exp. 2
PET* (pph)	100	100	100	100
CBC (pph)	0.7	0.7	0.7	0.7
Cl (ppm in CBC)	76	90	280	310
H ₂ O (ppm in CBC)	83	135	350	360
η_{rel}	1.82	1.80	1.73	1.70

* The relative viscosity of the starting material is 1.56

CLAIMS

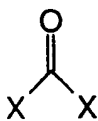
1. Process for the preparation of a carboxylic acid derivative according to the following general formula I:

5



Formula (I)

- where the fragments X are a lactam, an oxime or an imide in the form of HX, by mixing HX with phosgene, characterized in that hydrogen chloride is removed in gaseous form from the mixture formed.
2. Process according to Claim 1, in which HX is caprolactam.
3. Carbonylbiscaprolactam, characterized in that the water content is lower than 250 ppm and the chlorine content is lower than 300 ppm.
4. Carbonylbiscaprolactam, characterized in that the water content is lower than 150 ppm and the chlorine content is lower than 150 ppm.
5. Process for increasing the molecular weight of a polymer by mixing an –OH- or –NH₂-functional polymer in the melt with a carboxylic acid derivative according to formula I, characterized in that the carboxylic acid derivative has a water content of less than 250 ppm and contains less than 300 ppm chlorine.
6. Process according to claim 5, in which the carboxylic acid derivative has a water content of less than 150 ppm and contains less than 150 ppm chlorine.



Formule (I)

INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/NL 00/00879

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07D201/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, BEILSTEIN Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CHEMICAL ABSTRACTS, vol. 68, no. 23, 3 June 1968 (1968-06-03) Columbus, Ohio, US; abstract no. 104571, YO OKUDA ET AL: "N,N'-Carbonylbiscaprolactam" XP002143357 abstract & JP 42 017832 A (AJINOMOTO CO., INC.) 18 August 1967 (1967-08-18) cited in the application ---	1-6
A	EP 0 556 170 A (MONSANTO CO) 18 August 1993 (1993-08-18) claims 10-19 --- -/--	1-6

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

15 March 2001

Date of mailing of the international search report

18/04/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Chouly, J

INTERNATIONAL SEARCH REPORT

Intern. Application No.

PCT/NL 00/00879

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 972 237 A (TRIESELT WOLFGANG ET AL) 26 October 1999 (1999-10-26) the whole document, especially column 12 and column 23, example 6 ----	1-6
P,A	WO 00 17169 A (DSM NV ;LOONTJENS JACOBUS ANTONIUS (NL); PLUM BARTHOLOMEUS JOHANNE) 30 March 2000 (2000-03-30) the whole document -----	1-6

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Application No

PCT/NL 00/00879

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 42017832 A		NONE	
EP 0556170 A	18-08-1993	US 5200498 A	06-04-1993
US 5972237 A	26-10-1999	DE 19518039 A	21-11-1996
		DE 59604544 D	06-04-2000
		WO 9636686 A	21-11-1996
		EP 0826025 A	04-03-1998
		ES 2144246 T	01-06-2000
		JP 11505281 T	18-05-1999
WO 0017169 A	30-03-2000	NL 1010175 C	27-03-2000
		AU 6010099 A	10-04-2000